

Final Report

Heterogeneous Reactions on Aluminum Oxide
Surfaces Modeling Rocket Exhaust Particles

AFOSR Grant No. F49620-96-1-0029

Prof. Steven M. George, PI
Prof. Margaret A. Tolbert, co-PI

Dept. of Chemistry and Biochemistry
Univ. of Colorado
Boulder, CO 80309

20000308 003

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-00-

Public reporting burden for this collection of information is estimated to average 1 hour per response, in gathering and maintaining the data needed, and completing and reviewing the collection of information. collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, Paperwork Project, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Project, Suite 1204, Arlington, VA 22202-4302.

Sources,
et of this
Jefferson

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

3. REPORT TYPE AND DATES COVERED

FINAL 15 Jan 96 - 14 Jan 99

4. TITLE AND SUBTITLE

Heterogeneous Reactions on Aluminum Oxide Surfaces Modeling Rocket Exhaust Particles

5. FUNDING NUMBERS

F49620-96-1-0029

6. AUTHOR(S)

Dr. Steven M. George

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Colorado
Department of Chemistry and Biochemistry
Boulder CO 80309

8. PERFORMING ORGANIZATION
REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NL
801 N. Randolph Street, Rm 732
Arlington VA 22203-1977

10. SPONSORING/MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT

Approved for Public Release; Distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This research was performed by a graduate student, and post-doctoral research fellow. Our studies for the hydroxylation and dehydroxylation of α -Al₂O₃ (001) led to two publications. The adsorption of H₂O on α -Al₂O₃ (001) was accepted and published in the Journal of Physical Chemistry. The desorption of H₂O from α -Al₂O₃ (001) was accepted and published in Surface Science. The study of HCl adsorption and desorption from α -Al₂O₃ (001) led to one publication in Surface Science. In addition, the study of HCl and H₂O adsorption on α -Al₂O₃ (001) and the displacement of Al-OH surface species by HCl and displacement of Al-Cl surface species by H₂O led to one additional manuscript that is still under review. Since the conclusion of this research grant, we have continued to examine the surface chemistry of amorphous Al₂O₃ surfaces. Oxide surface chemistry is still a largely unexplored area. Our surface reactivity studies have helped to define this new territory in surface science. These studies have also improved our understanding of heterogeneous reactions on aluminum oxide rocket exhaust particles in the atmosphere.

14. SUBJECT TERMS

Hydroxylation, desorption, amorphous oxide

15. NUMBER OF PAGES

8

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

UNCLASS

18. SECURITY CLASSIFICATION
OF THIS PAGE

UNCLASS

19. SECURITY CLASSIFICATION
OF ABSTRACT

UNCLASS

20. LIMITATION OF
ABSTRACT

I. Program Objectives

During our support from the Air Force Office of Scientific Research, our research program has focused on heterogeneous reactions on Al_2O_3 surfaces that model the Al_2O_3 exhaust particles from solid-fueled rockets. Surface reaction kinetics and product formation were examined using laser induced thermal desorption (LITD) and temperature programmed desorption (TPD) studies on single-crystal $\text{Al}_2\text{O}_3(0001)$ surfaces. The research concentrated on the initial definition of the Al_2O_3 surface coverage after rocket firing and the heterogeneous reactions on the Al_2O_3 surfaces that emerge from the wake. This research should help to determine the effect of Al_2O_3 rocket exhaust on atmospheric chemistry.

Our main tasks in this research were to:

- Measure reactive sticking coefficients on the dehydroxylated Al_2O_3 surfaces that exist shortly after rocket firing. These experiments concentrated on H_2O and HCl sticking on the dehydroxylated $\alpha\text{-Al}_2\text{O}_3$ single-crystal surface.
- Determine the efficiency and extent of displacement of Al-OH surface species by HCl and Al-Cl surface species by H_2O on $\alpha\text{-Al}_2\text{O}_3$ single-crystal surfaces.
- Measure the reaction kinetics of CF_2Cl_2 , CF_2Br_2 and CCl_4 on the dehydroxylated $\alpha\text{-Al}_2\text{O}_3$ single-crystal surfaces for comparison with earlier results.
- Examine the reaction kinetics of CF_2Cl_2 , CF_2Br_2 , CCl_4 and CH_3CCl_3 on the hydroxylated, chlorinated and mixed (Al-OH & Al-Cl) $\alpha\text{-Al}_2\text{O}_3$ single-crystal surfaces.
- Measure the reaction kinetics of N_2O_5 , ClONO_2 and HOCl with the chlorinated and mixed $\alpha\text{-Al}_2\text{O}_3$ single-crystal surfaces.
- Determine the effect of heterogeneous reactions on Al_2O_3 surfaces on atmospheric chemistry. Assess the likelihood that Al_2O_3 exhaust particles could lead to stratospheric ozone depletion by activating chlorine in CFCs.

II. Program Achievements

During our funding for this program, we concentrated on the following topics:

- Preparation of a model single-crystal $\alpha\text{-Al}_2\text{O}_3(0001)$ surface for the proposed studies.
- Hydroxylation and dehydroxylation kinetics of the $\alpha\text{-Al}_2\text{O}_3(0001)$ single-crystal surface.
- Adsorption and desorption kinetics of HCl on the dehydroxylated $\alpha\text{-Al}_2\text{O}_3(0001)$ single-crystal surface.
- Temperature dependence of H_2O and HCl adsorption on the $\alpha\text{-Al}_2\text{O}_3(0001)$ single-crystal surface.
- Displacement of O-H surface species by HCl and displacement of Al-Cl surface species by H_2O .
- Growth of amorphous Al_2O_3 films by atomic layer deposition techniques
- Surface reactivity of amorphous Al_2O_3 films

This research was performed by a graduate student, Christine Nelson, and a post-doctoral research fellow, Jeff Elam. Christine Nelson graduated in December 1999 and recently started a new job at Intel Corporation in Hillsboro, Oregon. Jeff Elam is currently working on another research project in Steven George's Research Group.

Our studies for the hydroxylation and dehydroxylation of $\alpha\text{-Al}_2\text{O}_3(0001)$ led to two publications. The adsorption of H_2O on $\alpha\text{-Al}_2\text{O}_3(0001)$ was accepted and published in the *Journal of Physical Chemistry*. The desorption of H_2O from $\alpha\text{-Al}_2\text{O}_3(0001)$ was accepted and published in *Surface Science*.

Our study of HCl adsorption and desorption from $\alpha\text{-Al}_2\text{O}_3(0001)$ led to one publication in *Surface Science*. In addition, our study of HCl and H_2O adsorption on $\alpha\text{-Al}_2\text{O}_3(0001)$ and the displacement of Al-OH surface species by HCl and displacement of Al-Cl surface species by H_2O led to one additional manuscript that is still under review.

Since the conclusion of this research grant, we have continued to examine the surface chemistry of amorphous Al_2O_3 surfaces. Oxide surface chemistry is still a largely unexplored area. Our surface reactivity studies have helped to define

this new territory in surface science. These studies have also improved our understanding of heterogeneous reactions on aluminum oxide rocket exhaust particles in the atmosphere.

III. New Results from AFOSR Support

Our study of the hydroxylation of α - Al_2O_3 (0001) surfaces revealed that the initial sticking coefficient for H_2O on this α - Al_2O_3 surface is quite large with a magnitude of $S_0 \sim 0.1$ at 300 K. The H_2O sticking coefficient drops rapidly as a function of hydroxyl coverage and approaches $S \sim 10^{-10}$ at a hydroxyl coverage close to the saturation coverage of $0.5 \times 10^{15} \text{ cm}^{-2}$. Additional experiments with H_2^{18}O confirmed that the H_2O dissociated on the α - Al_2O_3 (0001) surface at 300 K. Equal quantities of H_2^{16}O and H_2^{18}O were observed in TPD experiments after exposing the α - $\text{Al}_2^{16}\text{O}_3$ (0001) surface to H_2^{18}O .

These adsorption results at 300 K predict that α - Al_2O_3 particles in the atmosphere will be hydroxylated with hydroxyl coverages of $\sim 0.24 \times 10^{15} \text{ cm}^{-2}$ after emerging from the rocket plume. Additional exposure to H_2O in the stratospheric ambient will increase the hydroxyl coverage to $\sim 0.30 \times 10^{15} \text{ cm}^{-2}$ before the particle falls out from the stratosphere. Consequently, the hydroxyl coverage is expected to be close to one monolayer.

We also determined the thermal stability of hydroxyl groups on α - Al_2O_3 (0001) surfaces. The removal of H_2O via recombinative desorption $\text{AlOH}^* + \text{AlOH}^* \rightarrow \text{Al-O-Al}^* + \text{H}_2\text{O(g)}$ occurs at temperatures between 300-500 K. Consequently, the hydroxyl coverage is negligible above 500 K. These results indicate that hydroxyl groups formed by the dissociative adsorption of H_2O at $T < 500 \text{ K}$ will be stable on Al_2O_3 particles at stratospheric temperatures of 185-210 K. These adsorption and desorption results indicate that reactions between fluorochlorocarbons and Al_2O_3 particles from rocket exhaust will occur on hydroxylated α - Al_2O_3 surfaces.

The broad range of desorption temperatures indicates that there are a variety of binding energy sites for O-H on α - Al_2O_3 (0001). H_2O desorption results versus coverage prepared by progressively annealing a fully reacted α - Al_2O_3 (0001) surface confirmed a wide range of binding energies. The TPD experiments also indicated that there is very low mobility for the O-H species on α - Al_2O_3 (0001). The TPD data showed that recombinatory H_2O desorption occurs from the original adsorption sites and that the initial H_2O adsorption randomly populates the various binding energy sites. Surprisingly, the O-H species do not appear to diffuse on the surface to find the lowest energy binding sites prior to thermal desorption.

Following the studies of the hydroxylation and dehydroxylation of α - $\text{Al}_2\text{O}_3(0001)$, we studied the adsorption and desorption of HCl on α - $\text{Al}_2\text{O}_3(0001)$. HCl is an important gas in the wake of solid rocket motors. HCl dissociative adsorption on Al_2O_3 particles may alter their reactivity with chlorofluorocarbons and affect the stratospheric ozone layer. We measured the HCl sticking coefficient on α - $\text{Al}_2\text{O}_3(0001)$ and observed an initial sticking coefficient of $S_0 \sim 10^{-3}$ at 300K. The HCl sticking coefficient decreased nearly exponentially versus the chlorine coverage. The HCl coverage saturated at an HCl coverage of $0.10 \times 10^{15} \text{ cm}^{-2}$ after HCl exposures of 10^{10} Langmuir. These HCl adsorption results indicate that α - Al_2O_3 rocket exhaust particles will be partially covered with O-H and Al-Cl surface species in the stratosphere.

HCl recombinative desorption also occurred over a wide temperature range from 300K to 650K. This broad temperature range indicates that there are a variety of binding energy sites for O-H and Al-Cl on α - $\text{Al}_2\text{O}_3(0001)$. HCl desorption results versus coverage prepared by progressively annealing a fully reacted α - $\text{Al}_2\text{O}_3(0001)$ surface confirmed a wide range of binding energies. The TPD experiments also indicated that there is very low mobility for the O-H and Al-Cl species on α - $\text{Al}_2\text{O}_3(0001)$. The TPD data showed that recombinatory HCl desorption occurs from the original adsorption sites and that the initial HCl adsorption randomly populates the various binding energy sites. Like the previous results following H_2O adsorption, the O-H and Al-Cl species do not appear to diffuse on the surface to find the lowest energy binding sites prior to thermal desorption. The HCl desorption results predict that O-H and Al-Cl surface species will be stable on Al_2O_3 rocket exhaust particles at stratospheric temperature and pressures.

The adsorption measurements for H_2O and HCl were performed initially on α - $\text{Al}_2\text{O}_3(0001)$ at 298K. The stratosphere has much colder temperatures of 180-220K. To determine the effect of temperature on the sticking coefficients, the uptake of H_2O and HCl was measured on α - $\text{Al}_2\text{O}_3(0001)$ at 210K. These measurements revealed that the lower temperature affected both the initial sticking coefficient on the clean α - $\text{Al}_2\text{O}_3(0001)$ surface and the sticking coefficient at higher O-H and Al-Cl surface coverages.

For H_2O , the initial sticking coefficient on α - $\text{Al}_2\text{O}_3(0001)$ was $S_0 \sim 10^{-1}$ at both 298K and 210K. However, the H_2O sticking coefficient did not decrease nearly as dramatically with surface coverage at 210K. At a coverage of $1 \times 10^{14} \text{ H}_2\text{O}/\text{cm}^2$, the sticking coefficient was $S \sim 1 \times 10^{-7}$ at 298K. At this same coverage at 210K, the sticking coefficient was $S \sim 1 \times 10^{-3}$. The temperature effects were even more dramatic for HCl adsorption. The initial sticking coefficient for HCl was $S_0 \sim 1 \times 10^{-3}$ at 298K and increased to $S_0 \sim 1 \times 10^{-1}$ at 210K. The effect of O-H and Al-Cl surface coverage on the HCl sticking coefficient also was much less at

210K. These temperature effects reveal that the Al_2O_3 rocket exhaust particles will be easily hydroxylated and chlorinated at stratospheric temperatures.

H_2O and HCl will be present simultaneously in the rocket exhaust wake and in the stratosphere. Consequently, O-H species on the Al_2O_3 surface could be displaced by HCl and Al-Cl species on the Al_2O_3 surface could be displaced by H_2O . These displacement reactions were confirmed by exposing a Al-Cl coverage on the $\alpha\text{-Al}_2\text{O}_3(0001)$ surface to H_2O . A H_2O exposure of 10^8L could replace $\sim 1/2$ of the Al-Cl surface species with O-H. Likewise, a O-H coverage on the $\alpha\text{-Al}_2\text{O}_3(0001)$ surface was exposed to a 10^9L HCl exposure. This HCl exposure replaced $\sim 1/3$ of the O-H surface species with Al-Cl. These experiments reveal that the surface coverage on Al_2O_3 particles may change and evolve with time depending on gas exposure.

Additional experiments explored new methods of depositing amorphous Al_2O_3 films. These amorphous Al_2O_3 films are representative of another class of Al_2O_3 rocket exhaust particles. The deposition of amorphous Al_2O_3 films was examined on tungsten and molybdenum surfaces using atomic layer deposition techniques. This method utilizes sequential exposures of $\text{Al}(\text{CH}_3)_3$ and H_2O to achieve the atomic layer control of Al_2O_3 film growth. Auger electron spectroscopy experiments revealed the layer-by-layer growth of continuous Al_2O_3 films. These amorphous Al_2O_3 films should be useful in future studies of Al_2O_3 surface chemistry.

IV. Personnel Supported

Faculty

1. Prof. Steven M. George
2. Prof. Margaret A. Tolbert

Postdoctoral Research Associates

1. Dr. Jeff Elam

Graduate Students

1. Christine Nelson

V. Publications

J.W. Elam, C.E. Nelson, M.A. Cameron, M.A. Tolbert and S.M. George, "Adsorption of H₂O on Single-Crystal α -Al₂O₃(0001) Surfaces", *J. Phys. Chem.* **B102**, 7008-7015 (1998).

C.E. Nelson, J.W. Elam, M.A. Cameron, M.A. Tolbert and S.M. George, "Desorption of H₂O from a Hydroxylated Single-Crystal α -Al₂O₃(0001) Surface", *Surf. Sci.* **416**, 341-353 (1998).

J.W. Elam, C.E. Nelson, M.A. Tolbert and S.M. George, "Adsorption and Desorption of HCl on a Single-Crystal α -Al₂O₃(0001) Surface", *Surface Science* (in press).

C.E. Nelson, J.W. Elam, M.A. Tolbert and S.M. George, "Effect of Temperature on H₂O and HCl Adsorption on Single-Crystal α -Al₂O₃(0001)", submitted to *Appl. Surf. Sci.*

VI. Interactions/ Transitions

The results from this research have been presented at various meetings and workshops around the country. A listing of these presentations is given below:

1. "Dehydroxylation and Rehydroxylation of α -Al₂O₃ Surfaces", S.M. George, M.A. Cameron, C.E. Nelson, M.A. Tolbert and S.M. George, National Symposium of the American Vacuum Society, Philadelphia, Pennsylvania, October 17, 1996.
2. "Adsorption and Desorption of H₂O on α -Al₂O₃(0001) Surfaces Modeling Rocket Exhaust Particles", C.E. Nelson, J.W. Elam, M.A. Tolbert and S.M. George, Rocky Mountain American Vacuum Society Meeting, Denver, Colorado, August 21, 1997.
3. "Adsorption and Desorption of HCl on α -Al₂O₃(0001) Surfaces Modeling Rocket Exhaust Particles", J.W. Elam, C.E. Nelson, M.A. Tolbert and S.M. George, Rocky Mountain American Vacuum Society Meeting, Denver, Colorado, August 21, 1997.
4. "Adsorption and Desorption of H₂O from α -Al₂O₃(0001)", S.M. George (INVITED), Symposium on Heterogeneous and Homogeneous Processes in Atmospheric Chemistry, National American Chemical Society Meeting, Las Vegas, Nevada, September 8, 1997.
5. "Adsorption and Desorption of H₂O on α -Al₂O₃(0001) Surfaces Modeling Rocket Exhaust Particles", J.W. Elam, C.E. Nelson, M.A. Tolbert and S.M. George, 44th Annual National Symposium of the American Vacuum Society, San Jose, California, October 20, 1997.
6. "Adsorption and Desorption of H₂O from α -Al₂O₃(0001)", S.M. George, Air Force Workshop on Atmospheric Effects of Rocket Exhaust, Beckman Center, Univ. of California, Irvine, California, January 9, 1998.

7. "Adsorption and Desorption of HCl from α -Al₂O₃(0001)", J.W. Elam, Air Force Workshop on Atmospheric Effects of Rocket Exhaust, Beckman Center, Univ. of California, Irvine, California, January 9, 1998.
8. H₂O Adsorption and Desorption Kinetics on α -Al₂O₃(0001)", S.M. George, Air Force Office of Scientific Research, Molecular Dynamics Review, Naval Postgraduate School, Monterey, California, May 18, 1998.
9. "HCl Adsorption and Desorption on a Single-Crystal α -Al₂O₃(0001) Surface, C.E. Nelson, J.W. Elam, M.A. Tolbert and S.M. George, Session on Oxide Surface Chemistry, 45th International Symposium of the American Vacuum Society, Baltimore, Maryland, November 5, 1998.

An invited talk on "Adsorption and Desorption Kinetics of H₂O on α -Al₂O₃ (0001)" was presented at the symposium on *Heterogeneous and Homogeneous Processes in Atmospheric Chemistry* at the National American Chemical Society Meeting in Las Vegas, Nevada on September 8, 1997. This presentation stimulated discussion and attracted the interests of several theoretical groups that are now modeling H₂O dissociative adsorption on α -Al₂O₃ (0001).

We have corresponded with several theorists who are modeling H₂O adsorption and desorption from α -Al₂O₃(0001). One theorist is Dr. Eugene Stefanovich and his theoretical group in the Dept. of Chemistry at the Univ. of Utah. They are modeling H₂O adsorption on α -Al₂O₃ (0001). Another theorist who is modeling H₂O adsorption on α -Al₂O₃(0001) is Prof. William Hase in the Dept. of Chemistry at Wayne State University.

VII. Inventions or Patent Disclosures

NONE

VIII. Honors/Awards

Prof. Steven M. George was elected a fellow in the American Physical Society (Fall 1997). He also has received the Presidential Young Investigator Award (1988-1993), the Alfred P. Sloan Foundation Award (1988), an IBM Faculty Development Award (1988), a Dreyfus Award for Newly Appointed Faculty in Chemistry (1985) and an AT&T New Faculty Award (1985).

Prof. Margaret A. Tolbert received the National Science Foundation Young Investigator Award (1992-1996), the AAAS Newcomb Cleveland Award (1987), the James B. Maccelwane Medal (1993) and the Camille Dreyfus Teacher-Scholar Award (1994). She is also a fellow of the American Geophysical Union (1993).